Catalyst Active Sites Imaged in Real Time

Three Empty Pd Sites Break H_2 Molecules, Two Don't

As reported in a recent issue of *Nature*, a group led by Miquel Salmeron has captured the atomic-scale formation and dynamics of "active sites" on a catalytic surface for the first time. Using movies made from a time series of Scanning Tunneling Microscope (STM) images, the researchers observed the behavior of the sites on the surface of palladium metal (Pd) to which diatomic hydrogen gas (H_2) can be adsorbed and then dissociated into two H atoms (dissociative adsorption). It was found, contrary to the prevailing view, that three empty surface sites are required for this process to occur—two empty sites are not sufficient.

Under reaction conditions, a catalyst surface interacts with a constantly fluctuating mix of reactants, products, "spectators" that do not participate in the reaction, and species that either promote or inhibit the activity of the catalyst. The detailed mechanism by which molecules adsorb to and dissociate from this surface under such dynamic conditions is often poorly understood. An example is the dissociative adsorption of the diatomic molecule H_2 which occurs on a number of noble metal surfaces and is a central step in many industrial processes. It had generally been assumed that this reaction requires at least two adjacent and empty atomic adsorption sites (which, from the point of view of an H-saturated surface, can be considered H vacancies) for an impinging H_2 molecule to stick to the surface and dissociate into its two H atoms. However, this conjecture had never been proved experimentally.

The LBNL team addressed this question by using Scanning Tunneling Microscopy to observe the catalyst surface with atomic resolution. To perform the experiments the researchers had to slow the reaction and the diffusion of the atoms by cooling the surface to 37K. STM images were obtained at 75 second intervals and linked to make a movie. Under the imaging conditions, empty sites (H vacancies) appear as bright spots (see figure). When the temperature was raised to 50 K to allow diffusion, H vacancies on the nearly saturated surface appeared to be hopping randomly, occasionally creating vacancy clusters with 2, 3, or more sites. (It is actually the H atoms that are moving. The positions they vacate are the "H vacancies" and because their bright spots are what are observed, it is convenient to talk of them rather than the H atoms as "moving.") The motions of the various vacancy clusters were then followed carefully in the presence of a flux of H_2 gas. Clusters created when two vacancies near each other appear as 3-site triangles because the two vacancies "hop" among the three sites so quickly that all three show as bright. They were observed to move around the surface, but the adsorption of H_2 (which would have instantaneously annihilated the site) was not observed. Instead, these vacancy pairs eventually separated into individual vacancies. In contrast, molecules from the gas phase did adsorb at triangular-appearing clusters which are formed when of three or more vacancies approach each other. Again these appear as six (or more) bright spots because the three (or more) vacancies hop among six sites. This adsorption could be observed directly as the number of vacancies in the cluster was reduced by 2 (see figure). The obvious implication of this observation is that that two empty Pd sites are not sufficient for the binding and dissociation of H_2; at least three sites are required.

This surprising result calls into question the conventional thinking on the structure of active sites on catalyst surfaces. Further real-time measurements are underway that will help to improve the molecular-level understanding of the formation of the active sites that determine the activity of catalytically active surfaces.

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T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, "Dissociative hydrogen adsorption on palladium requires aggregates of three or more vacancies," *Nature* **422**, 705 (2003)